Chemical Structure and Upconversion Enhancement of $NaYF_4$ Nanocrystals and Nanosheets

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BSc (Hons)

A thesis submitted in partial fulfilment of requirements for the degree of Doctor of Philosophy

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July 2020

Declaration of Authorship

I, Christian Clarke, declare that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also declare that the work presented is my own and the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis has been acknowledged. In addition, I declare that all information sources and literature used are indicated in the thesis.

This research is supported by the Australian Government Research Training Program.

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Date: 2/7/2020

Acknowledgements

I would first like to thank my supervisory team consisting of A/Prof. Cuong Ton-That, Dr Xiaoxue Helen Xu and Prof. Dayong Jin. All have gone above and beyond, I simply could not ask for better supervisors. Thank you for your continued advice, support and hard work throughout our journey together. I want to specifically thank Cuong for introducing me to synchrotron soft X-ray characterisation an invaluable skill I now have, Helen for her lively discussions with fresh perspectives and Jin for welcoming me to IBMD with generous opportunities and international experience.

Thank you to all members of IBMD in particular: Dr Deming Liu and Dr Chenshuo Ma for kindly providing me with my first UCNPs; Dr Fan Wang, Mr Yongtao Liu, Mr Chaohao Chen and Mr Yunfei Shang for their optical abilities and knowledge; and Dr Jiajia Zhou for the opportunity of collaboration in contributing to your outstanding research.

For all the technical staff at UTS Mr Mark Berkahn, Mr Geoff McCredie, Mr Herbert Yuan, Dr Angus Gentle, Mrs Katie McBean, Dr Linda Xiao, Mr Alex Angeloski and Dr Ronald Shimmon I would like to thank you for your assistance and training with equipment.

To the Australian Synchrotron soft X-ray spectroscopy beamline scientists Dr Bruce Cowie, Dr Anton Tadich and Dr Lars Thomsen thank you for passing on not only your expertise but also your passion for synchrotron characterisation to me.

RMIT collaborators Dr Vipul Bansal and Dr Mandeep Singh, together we envisioned a new material and made it a reality, without our collaboration this would not be the case, for this I sincerely thank you. I would particularly like to distinguish Dr Sherif Tawfik as the source of the initial inspiration for this project and for his tireless work on the crucial simulations.

Dr Noushin Nasiri thank you for introducing me to the world of breath sensors and flame spray pyrolysis. I am grateful to have been involved in your work and am looking forward to all your future research.

Many thanks to the Australian Government as a recipient of a Research Training Program Scholarship.

Finally, to my friends and family Alex Gee, Ling Ling Chan, Allen Zhou, Matt Cappadonna, Ziqing Miriam Du and my parents Anthony Clarke and Kathryn Clarke, thank you for your unconditional support throughout this time.

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List of Acronyms

AFM	Atomic Force Microscopy
CCD	Charged Couple Device
CET	Cooperative Energy Transfer
CS	Core Shell
DFT	Density Functional Theory
EDS	Energy-dispersive X-ray Spectroscopy

EMU	Energy Migration Upconversion
ESA	Excited State Absorption
ETU	Energy Transfer Upconversion
FFT	Fast Fourier Transform
HTCP	High Temperature Co-Precipitation
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IMFP	Inelastic Mean Free Path
LSPR	Local Surface Plasmon Resonance
ML	Monolayer
$NaYF_4$	Sodium Yttrium Fluoride
NEXAFS	Near Edge X-ray Adsorption Fine Structure
NIR	Near-infrared
OA	Oleic Acid
ODE	1-Octadecene
OM	Oleylamine
PA	Photon Avalanche
PDOS	Partial Density of States
PEY	Partial Electron Yield
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)
RE	Rare Earth
SCCM	Standard Cubic Centimetre per Minute
SEM	Scanning Electron Microscopy
SLTD	Solid-Liquid-Thermal-Decomposition
SPAD	Single Photon Avalanche Diode
TCD	Thermal Co-Decomposition

TEA	Triethylamine
TEM	Transmission Electron Microscopy
TEY	Total Electron Yield
TFY	Total Fluorescent Yield
UCNP	Upconversion Nanoparticle
UV-Vis	Ultraviolet Visible
VASP	Vienna Ab initio Simulation Package
XRD	X-ray Powder Diffraction
XPS	X-ray Photoelectron Spectroscopy

List of Publications

Journal Publications

1. Xiaoxue Xu, **Christian Clarke**, Chenshuo Ma, Gilberto Casillas, Minakshi Das, Ming Guan, Deming Liu, Li Wang, Anton Tadich, Yi Du, Cuong Ton-That, Dayong Jin. "*Depth-profiling of Yb^{3+} sensitizer ions in $NaYF_4$ upconversion nanoparticles*" 2017, Nanoscale 9 (23) 7719-7726. [1]

2. Jiajia Zhou, Shihui Wen, Jiayan Liao, **Christian Clarke**, Sherif Abdulkader Tawfik, Wei Ren, Chao Mi, Fan Wang, Dayong Jin. "*Activation of the surface dark-layer to enhance upconversion in a thermal field*" 2018, Nature Photonics 12 (3), 154. [2]

3. **Christian Clarke**, Deming Liu, Fan Wang, Yongtao Liu, Chaohao Chen, Cuong Ton-That, Xiaoxue Xu, Dayong Jin. "*Large-scale dewetting assembly of gold nanoparticles for plasmonic enhanced upconversion nanoparticles*" 2018, Nanoscale 10 (14), 6270-6276. [3]

4. Wei Ren, Gungun Lin, **Christian Clarke**, Jiajia Zhou, Dayong Jin. "*Optical Nanomaterials and Enabling Technologies for High-Security-Level Anticounterfeiting*" 2019, Advanced Materials 32(18), 1901430. [4]

5. Du Ziqing, Abhishek Gupta, **Christian Clarke**, Matt Cappadona, David Clases, Deming Liu, Zhuoqing Yang, Shawan Karan, William Price, Xiaoxue Xu. "*Porous upconversion nanostructures as bimodal biomedical imaging contrast agents*" 2020, Journal of Physical Chemistry C, 124, 22, 12168–12174. [5]

6. Noushin Nasiri, **Christian Clarke**. "*Nanostructured Chemiresistive Gas Sensors for Medical Applications*" 2019, Sensors 19.3: 462. [6]

7. Noushin Nasiri, **Christian Clarke**. "*Nanostructured Gas Sensors for Medical and Health Applications: Low to High Dimensional Materials*" 2019, Biosensors 9(1), 43. [7]

(1 - 5 are closely related to my PhD program)

Oral Presentations

Xiaoxue Xu, **Christian Clarke**, Chenshuo Ma, Gilberto Casillas, Minakshi Das, Ming Guan, Deming Liu, Li Wang, Anton Tadich, Yi Du, Cuong Ton-That, Dayong Jin. "Depth-profiling of Yb^{3+} sensitizer ions in $NaYF_4$ upconversion nanoparticles" ICONN 2018, Wollongong, February 2018.

Abstract

The ability of lanthanide ions to convert lower energy photons to higher energy photons through the process known as upconversion presents as an opportunity to overcome limitations in sensitivity, efficiency and selectivity present for a wide variety of applications such as bio-imaging, photovoltaics and anti-counterfeiting.

Sodium Yttrium Fluoride ($NaYF_4$) is an inorganic insulator with low phonon energy (360 $cm^{-1} \approx 45$ meV), wide band gap (8.5 eV) and high chemical stability. These properties make $NaYF_4$ an ideal optical host crystal for lanthanide dopants to produce upconversion nanoparticles (UCNPs). The shape, size and structure of UCNPs can be highly controlled allowing them to be tailored to the requirements of specific applications.

Key challenges of concentration quenching and low quantum yield still confront UCNPs before their potential can be fully realised. Accordingly, enhancing the efficiency of UCNPs and their brightness has been the focus of numerous studies. In this project these challenges facing UCNPs are addressed by material characterisation and optimisation based on a comprehensive understanding of the chemical and optical properties of the material.

Firstly, synchrotron-based XPS and NEXAFS along with EDS and ICP-MS characterisation techniques were employed on a range of UCNPs with sizes from 13 nm - 51 nm and different lanthanide (Ln^{3+}) concentrations of 20% - 60% to determine how lanthanides are distributed within each nanocrystal. This analysis reveals a radial gradient distribution of Yb^{3+} and Tb^{3+} exists from the core to the surface of the $NaYF_4$ UCNPs, regardless of their size or lanthanide dopant concentration. The active core structure of this distribution was then systematically correlated to the optical properties of UCNPs with different sizes revealing a trend of increased optical upconversion emission efficiency by smaller sized UCNPs.

Secondly, surface plasmon coupling was achieved between core-shell UCNPs and dewetted gold nanoparticles by precisely growing $NaYF_4$ shell coatings of varied thickness from 5 nm - 15 nm around the optically active core UCNPs. The local

surface plasmon of the gold nanoparticles could be controlled and coupled with the internal transitions of the Er^{3+} ions. Combining these inert shelled UCNPs and plasmonic gold nanoparticles produced a shell thickness dependent enhancement with five times enhanced upconversion emission from the core-shell UCNPs with a shell thickness of 10 nm.

Thirdly, bulk $NaYF_4$ microparticles were successfully exfoliated to make 2D $NaYF_4$ nanosheets. By using a simple soft exfoliation method without the need for intensive ultrasonication atomically flat optically active nanosheets down to a single monolayer were produced. Extensive characterisation of the nanosheets supported by DFT calculations reveals a phase change and 1 eV band gap reduction for this new 2D material compared to the bulk.

Finally, in an appendix to demonstrate a massive three orders of magnitude increase in emission from ultra-small Tm^{3+} doped UCNPs an anti-counterfeiting mark was designed and fabricated. This enhancement only occurs at high temperature as activated surface phonons become efficient energy pathways for energy migration. The temperature dependence of the enhancement allowed the anti-counterfeiting mark to be temperature responsive.